HYDROGEN PRODUCTION FROM WATER REDUCTION PROCESS OVER Ni SUPPORTED ON SILICA CATALYSTS

KITTIPONG PRAKOBTHAM
KHWANNETE KITYUNYOUNG
NACHAPATT RIENNARUMOLPORN

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR
THE DEGREE OF BACHELOR OF SCIENCE (INDUSTRIAL CHEMISTRY)
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
ACADEMIC YEAR 2015

การผลิตก๊าซไฮโดรเจนจากปฏิกิริยารีดักชันของน้ำโดยใช้ตัวเร่งปฏิกิริยาโลหะนิกเกิลบนตัวรองรับซิลิกา

HYDROGEN PRODUCTION FROM WATER REDUCTION PROCESS OVER Ni SUPPORTED ON SILICA CATALYSTS

กิตติพงษ์ ประกอบธรรม

ขวัญเนตร กิจยรรยง

ณชพรรธน์ เหรียญนฤมลพร

โครงงานพิเศษนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
ปริญญาวิทยาศาสตรบัณฑิต (เคมีอุตสาหกรรม)
ภาควิชาเคมี คณะวิทยาศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
ปีการศึกษา 2558

Title	Hydrogen production from water reduction process over Ni supported on silica catalysts
Students	Mr. Kittipong Prakobtham Student ID 55050575
	Miss Khwannete Kityunyoung Student ID 55050586
	Mr. Nachapatt Riennarumolporn Student ID 55050635
Degree	Bachelor of Science (Industrial Chemistry)
Department	Chemistry
Faculty	Science
University	King Mongkut's Institute of Technology Ladkrabang (KMITL)
Academic Year	2015
Advisor	Assoc. Prof. Dr. Tawan Sooknoi

Faculty of Science, King Mongkut's Insitute of Technology Ladkrabang (KMITL), has approved this special project submitted in partial fulfillment of the requirement for the degrees of Bachelor of Science (Industrial Chemistry) in academic year 2015.

Committees	Signatures
Asst. Prof. Dr. Montree Thongkam Chairperson	
Dr. Karoon Sadorn Committee	Karoon Sadorn
Assoc. Prof. Dr. Tawan Sooknoi Committee and Advisor	

Title	Hydrogen production from water reduction process over Ni supported on silica catalysts
Students	Mr. Kittipong Prakobtham Student ID 55050575
	Miss Khwannete Kityunyoung Student ID 55050586
	Mr. Nachapatt Riennarumolporn Student ID 55050635
Degree	Bachelor of Science (Industrial Chemistry)
Department	Chemistry
Faculty	Science
University	King Mongkut's Institute of Technology Ladkrabang (KMITL)
Academic Year	2015
Advisor	Assoc. Prof. Dr. Tawan Sooknoi

Abstract

Propionaldehyde is a role model of aldehydes and it is obtained from glycerol that is a low-value by-product from the biodiesel process. Moreover, most sugars are derivatives of aldehydes. The conversion of propionaldehyde to more valuable products such as hydrogen and propionic acid are interested. In this research, the water reduction of propionaldehyde to propionic acid and hydrogen over Ni/SiO_2 catalyst was attempted. However, ethylene and 1-propanol are observed in parallel. Ethylene is formed by decarbonylation of propionaldehyde, particularly over the catalyst with large particle size and at high temperature. 1-Propanol can be produced from hydrogenation of propionaldehyde with H_2, largely produced from water reduction and decarbonylation. The optimum temperature for water reduction of propionaldehyde is found at 195°C. The results suggest that 5% wt. Ni/SiO_2 provided high selectivity to propionic acid and hydrogen due to the small Ni particle size with high $Ni\text{-}SiO_2$ interface. While, 10%, 15%, and 20% wt. Ni/SiO_2 catalysts possess large Ni particle size and provide a similar product selectivity. The observed activity is derived from only the Ni metal on the surface, not from the nickel silicate species.

Keywords: water reduction, hydrogen production, Ni supported on silica catalysts

ACKNOWLEDGEMENTS

The authors wish to gratefully thank our advisor, Assoc. Prof. Dr. Tawan Sooknoi for the supervision, inspiration, suggestions, and encouragement throughout this research. This thesis would not have been completely finished without his advisory and supports.

We are grateful to thank Asst. Prof. Dr. Montree Thongkam and Dr. Karoon Sadorn for serving as the committees and their valuable comments.

We would like to appreciate the support from the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang for the equipment, chemicals, and facilities.

Special thanks go to our laboratory seniors, Mr. Thanasak Solos for his kindness and informative answers to the questionnaires.

Finally, we deeply appreciate and thank to our parent, our beloved friends, and whose name not mentioned here for all of their support throughout the period of this research.

Kittipong Prakobtham
Khwannete Kityunyoung
Nachapatt Riennarumolporn

CONTENTS

Page

CONTENTS (CONTINUED)

CONTENTS (CONTINUED)

LIST OF TABLES

Table Page

LIST OF SCHEMES

Scheme Page

LIST OF FIGURES

Figure **Page**

CHAPTER 1
INTRODUCTION

1.1 Motivation

Nowadays, the demand of petroleum fuel and energy usage increases steadily due to an expansion of economy; while, the source of fossil fuel depletes steadily. Therefore, alternative energy is required to replace petroleum fuel. One of the most interesting is hydrogen energy, which is considered as a renewable energy, cleanness, environmental friendly and combustion without greenhouse gases which cause global warming. Hydrogen is the simplest element. An atom of hydrogen consists of only one proton and one electron. It is also the most plentiful element in the universe. Despite it is simplicity and abundance, hydrogen does not occur naturally as a gas on the earth but it is always combined with other elements. For example, water is a combination of hydrogen and oxygen (H_2O). Hydrogen is also found in many organic compounds, notably the hydrocarbon that makes up many of fuels, such as gasoline, natural gas, methanol, and propane. Currently hydrogen production is obtained from several technologies; an electrical current can also be used to separate water into its components of oxygen and hydrogen. This process is known as electrolysis, which produces very pure hydrogen but still high production cost. Moreover, hydrogen can be produced from hydrocarbon via steam reforming process, the current leading technology for producing hydrogen in large quantities. However, this reaction causes a side production of carbon dioxide and carbon monoxide, which are greenhouse gases and contribute to global warming. Thus the low production cost and environmental friendly method for hydrogen production becomes the topic of interest, i.e., the water reduction process

The water reduction process, this process is studied on aldehyde transformation to carboxylic acid and hydrogen via reduction followed by dehydrogenation over acidic catalyst. The reduction in the presence of water yields germinal-diol formation as an intermediate over acidic catalyst and subsequent rapid dehydrogenation to the carboxylic acid as a main product and hydrogen as a byproduct [1]. The dehydrogenation of diol formed can be promoted by active metal catalysts, such as palladium, silver, nickel, and platinum over various inert supports, such as silica [2].

Nickel is typically used as a catalyst for dehydrogenation because it is common and relatively cheaper than palladium and platinum. Propionaldehyde is a role model of aldehydes that it is more soluble in water than higher aldehyde and it is obtained from glycerol via acrolein [3].

In this study, the conversion of propionaldehyde to propionic acid is investigated in a continuous fixed-bed reactor. Nickel supported on silica is used as a catalyst. The reaction conditions in catalytic bed reactor were fixed 1 atm and contact time in range of 250-500 g.h/mol. The effect of nickel loading (in % wt.), temperature and contact time in catalytic bed on the activity and selectivity towards propionic acid is investigated in this research.

1.2 Objectives

1) To produce propionic acid and hydrogen from propionaldehyde using continuous fixed-bed reactor (Ni supported on SiO_2 catalysts)
2) To understand the effect of nickel loading (in % wt.), temperature and contact time on the activity and selectivity of the catalyst
3) To understand the mechanism of the conversion of propionaldehyde to propionic acid
4) To explain deactivation behavior of the catalyst

1.3 Scope of Study

The scopes of this special project are as follows:

1) Preparation of catalyst by wetness impregnation: 5, 10, 15, 20% wt. nickel on silica (Ni/SiO_2)
2) Characterization of the prepared catalyst by Temperature Programmed Reduction (H_2-TPR)
3) Study on nickel loading in a range of 5-20% wt. with contact time between 250-500 g.h/mol and temperature in range of 165-220°C to evaluate the catalytic activity and selectivity in a continuous fixed-bed system of those reaction conditions
4) Analysis of liquid products by Gas Chromatography with Flame Ionization Detector (GC-FID)

1.4 Expected results

It is expected that a new technology for producing propionic acid and hydrogen from propionaldehyde will be obtained and developed with higher efficiency.

CHAPTER 2
THEORY AND LITERATURE REVIEWS

2.1 Propionaldehyde

2.1.1 Propionaldehyde information

Propionaldehyde is a chemical, also known as propanal, is a colorless, flammable liquid with a sharp and suffocating odor. It occurs naturally in vegetables such as onions and in some dairy products. Propionaldehyde is highly reactive and occurs as a chemical intermediate when preparing C-3 and C-6 compounds. There is no direct use of propionaldehyde but it is primarily converted into 1-propanol, propionic acid and thrimethylolethane, which are used in the manufacture of plastics, in the synthesis of rubber chemicals, as a metabolism of pharmacology, as a disinfectant and as a preservative in industries.

2.1.2 Properties of propionaldehyde

Propionaldehyde is an organic compound with the chemical formula of CH_3CH_2CHO (C_3H_6O). It is synonymous to propanaldehyde, propanal, propyl aldehyde, methyl acetaldehyde and propionic aldehyde. Propionaldehyde is a saturated three carbon chains with formyl group or aldehyde group and is an isomer of acetone as shown in Figure 2.1

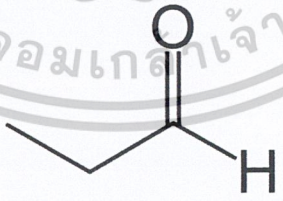


Figure 2.1 Structure of propanaldehyde

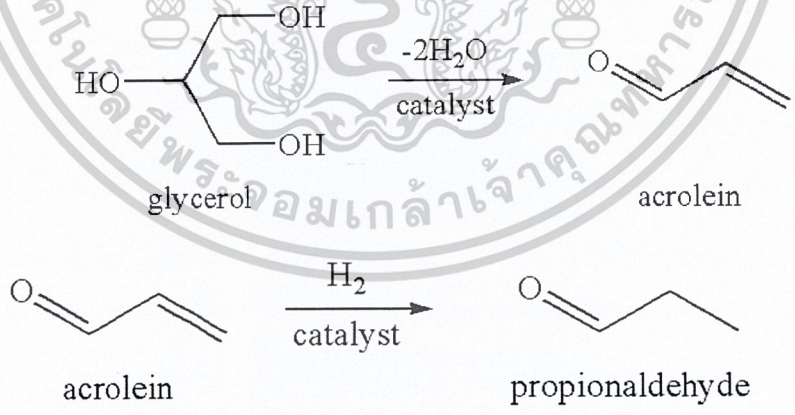
Physically, propionaldehyde is a clear colorless liquid with an overpowering fruity and suffocating odor. The boiling point, melting point and flash point of propionaldehyde is 49°C, -81°C, and -30°C respectively. Under normal atmospheric

pressure, propionaldehyde has a molecular weight of 58.08 g/mol, a density of 0.81 g/cm^3, solubility in water of 20 g/100mL, also in ethanol and diethyl ether. A viscosity of propionaldehyde is 6x10^{-4} Pa.s at 20°C. Propionaldehyde is highly flammable, very reactive in nature, easily oxidized or reduced, may form explosive peroxides and incompatible with strong bases and strong reducing agents. It is vigorous polymerization reaction with methyl methacrylate.

2.1.3 Source of propionaldehyde

Propionaldehyde is produced by using different manufacturing processes including preparation by treating propyl alcohol with a dichromate oxidizing mixture, synthesis by dry distillation of barium propionate with calcium formate and by hydroformylation. In the hydroformylation process, propionaldehyde is produced by combining ethylene and synthesis gas using a metal, especially rhodium, as a catalyst.

In addition, a previous study has shown that a new process developed by Biofuel-solutions for production of propionaldehyde from glycerol. The general concept is to react glycerol together with hydrogen at the secondary hydroxyl over catalysts to first form acrolein by dehydration and then followed by hydrogenation of acrolein to propionaldehyde as a product finally [3,4], presented in Figure 2.2.



Scheme 2.1 Reaction pathway of glycerol to propionaldehyde [5]

2.1.4 Used of Propionaldehyde

Propionaldehyde is mainly used in the production of cosmetics, personal care products and basic chemicals. The application products of propionaldehyde are used in several end-user industries such as chemicals, personal care and pharmaceuticals. In the chemicals industry, propionaldehyde is used for manufacturing basic chemicals, organic chemicals, agricultural chemicals, pesticides and fertilizers. In the home and personal care industry, propionaldehyde is used for the manufacturing of aroma chemicals that are used in preparing fragrances and perfumes. In the pharmaceutical industry, propionaldehyde is used in the production of basic pharmaceutical products. The growing demand from chemicals, personal care and pharmaceuticals industry is expected to drive the global propionaldehyde market in the next few years.

Propionaldehyde is basically a chemical intermediate used in the production of propionic acid and alkyd resins. Propionaldehyde finds use in a wide range of applications such as intermediates, plasticizers, plastics, lacquers, flavorings, perfumes, rubber chemicals, polyhydric alcohols or polyols. and cellulose. The demand for all these application products, especially fertilizers and pesticides, is growing significantly across the globe. The demand for fertilizers and pesticides is increasing across the world due to the need to achieve better agriculture yield amidst the influence of factors such as rising global population and decreasing arable land. This is ultimately resulting in the growth in demand for propionaldehyde in the manufacturing of fertilizers and pesticides. Hence, the growth in the fertilizers industry is one of the important factors which will create a positive impact on the global propionaldehyde market in the near future.

Asia Pacific is expected to be the fastest growing market for propionaldehyde in the next six years. This growth can be attributed to the rising demand for pesticides, fertilizers, personal care products and pharmaceutical products, typically in China, India and South East Asian countries. The population in these countries is increasing at a rapid rate. Moreover, owing to the economic development of these countries, the disposable income of the consumers is increasing. This subsequently results in an increase in the number of potential consumers across these developing countries. Furthermore, the other emerging economies such as Brazil, South Africa, Saudi Arabia [6].

2.2 Ni supported on silica catalyst

Heterogeneous transition metal catalysts for dehydrogenation are usually employed in the states of metal, oxides, or sulfides that are either unsupported or supported. The physical form of a catalyst suitable for a particular dehydrogenation is determined primarily by the type of reactors, such as fixed-bed, fluidized-bed, or batch reactor. For industrial purpose, unsupported catalysts are seldom employed since supported catalysts have many advantages over unsupported catalysts. In general, use of a support allows the active component to have a larger exposed surface area, which is particularly important in those cases, where a high temperature is required to activate the active component. At that temperature, it tends to lose its high activity during the activation process, such as in the reduction of nickel oxides with hydrogen, or where the active component is very expensive as are the cases with platinum group metals. The effect of an additive or impurity appears to be more sensitive for unsupported than supported catalysts. This is also in line with the observations that supported catalysts are usually more resistant to poisons than unsupported catalysts. Supported catalysts may be prepared by a variety of methods, depending on the nature of active components as well as the characteristics of carriers. An active component may be incorporated with a carrier in various ways, such as, by decomposition, impregnation, precipitation, co-precipitation, adsorption, and ion exchange.

Supported metal catalysts, particularly metals supported on SiO_2, which well-known that high surface area catalyst, have attracted considerable attention due to the importance of the silica–metal interface in heterogeneous catalyst because the size and nature of the interaction of a metal particle with an oxide support are critical in determining catalytic activity and selectivity [7-9]. It has been shown that metals supported on SiO_2 exhibit a metal–support interaction that varies from weak to strong depending upon the metal, temperature treatments and pressure [10]. Active metal catalysts, such as palladium, silver, nickel, and platinum. Nickel is typically used as a catalyst because it is common and relatively cheaper than palladium and platinum.

2.2.1 The used of nickel as a catalyst

In organic chemistry, Ni catalytic hydrogenation and dehydrogenation of organic compounds is a very common reaction. In particular, nickel powders have many important industrial applications. They are commonly used in alkaline rechargeable batteries, magnetic recording media and chemical catalysts [11]. Nickel is a very active metal in dehydrogenation catalysis. It is also a cheap element, thus, allowing its use as a bulk metal as well as in the form of highly loaded supported catalysts. This also rises to sulfur resistance, just because much sulfur is needed to fully poison highly loaded catalysts [12]. Moreover, nickel catalyst plays a central role in many synthetic transformations in which carbon-carbon bonds are formed to the reduction of electron rich carbon bonds with nickel catalysts. There are many of papers and patents published on the use of nickel as a catalyst for the dehydrogenation of organic compounds especially with regard to selective reaction, i.e., the modification of the proportion of simultaneous reactions through control of the temperature, pressure, reaction and character of the catalyst [13]. These nickel catalysts span a range of oxidation states: Nickel (0), nickel (II), nickel (III) and nickel (IV).

Many investigators have recognized that nickel oxide supported on kieselguhr gives much more activity catalysts than an unsupported one; although, the reduction temperature of supported oxide required in the range of 350–500°C [14].

2.2.2 The used of silica as a catalyst support [15]

In chemistry, a catalyst support is the material usually a solid with a high surface area. The reactivity of heterogeneous catalysts occurs at the surface atoms. Consequently, great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica. Silica supported, it is well-known that high surface area and was studied in this field with nickel catalyst.

In nature, silica can be found in a wide range of both crystalline and amorphous structures depending on the previous history of the sample. In all cases, the structure involves the connection of tetrahedral SiO_4 units so that different polymorphs showing the different relative orientation and coordination. This permits one to use cluster models to simulate SiO_2 surfaces since the different structures differ essentially in the long range order which lead to the different crystalline and amorphous forms of silica. Additionally, the largely covalent character of this oxide facilitates a very simple representation by means of cluster models. In this case, part of the material is cut from the bulk of the most common polymorph at ambient conditions, this being the alpha phase. This cut leads a series of dangling bonds either at silicon or at the oxygen atoms. Usually O atoms are preferred at the cluster edge since in this case the resulting dangling bond can be more realistically saturated by embedding hydrogen atoms. This is because the H electronegativity is relatively close to that of Si. The alternative option leads to unrealistic Si-H bonds, which strongly and artificially polarizes the rest of the material model. The orientation chosen for these embedded H atoms is in the line of the O-Si bond cut at atypical O-H bond. Furthermore, these terminal or capping atoms are kept fixed so as to reproduce the mechanical restrictions induced by the rest of the solid matrix. This strategy is commonly used to simulate other materials such as silicon or zeolites and has been reviewed at length by various authors. According to the weak dispersing ability of silica, Ni on silica gives rise to Ni-metal particles weakly interacting with this quite inert "support".

2.3 Propionic acid

2.3.1 Propionic acid information

Propionic acid was first described in 1844 by Johann Gottlieb, who found it among the degradation products of sugar. Over the next few years, other chemists produced propionic acid in various other ways, none of them realizing they were producing the same substance. In 1847, the French chemist Jean-Baptiste Dumas established all the acids to be the same compound, which he called propionic acid, from the Greek words protos meaning first and pion meaning fat, because it is the smallest $H(CH2)_nCOOH$ acid that exhibits the properties of the other fatty acids, such as producing an oily layer when salted out of water and having a soapy potassium salt.

2.3.2 Properties of propionic acid

Propionic acid is an organic compound with the chemical formula of CH_3CH_2COOH. It is synonymous to propanoic acid, ethylformic acid, methyl acetic acid, carboxyethane and also known as ethane carboxylic acid. Propionic acid is a saturated three-carbon chain with naturally carboxylic acid as a functional group, shown in Figure 2.9

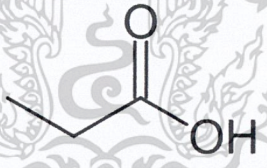


Figure 2.2 Structure of propionic acid

Physically, propionic acid is a colorless liquid with a sharp rancid and pungent odor. The boiling point, melting point and flash point of propionic acid is 141°C, -21°C, and 54°C respectively. Under normal atmospheric pressure, propionic acid has a molecular weight of 74.08 g/mol, a density of 0.99 g/cm^3, solubility in water very good and all normal organic solvents, but can be removed from water by adding salt. Propionic acid has physical properties intermediate between those of the smaller carboxylic acids, formic and acetic acids, and the larger fatty acids. Propionic acid displays the general properties of carboxylic acids: It can form amide, ester, anhydride, and chloride derivatives.

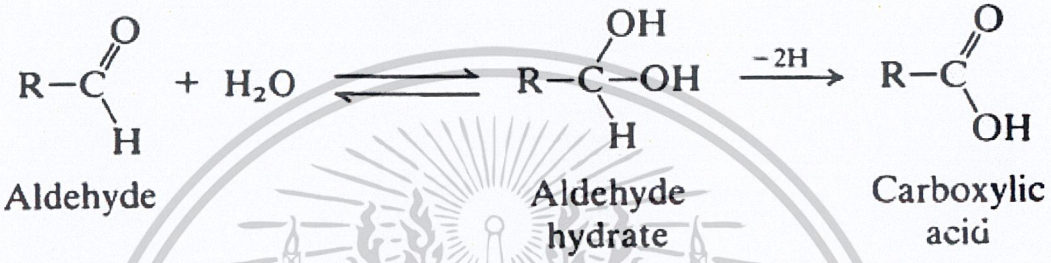
2.3.3 Used of propionic acid

As a result shown in figure 2.10, most propionic acid is consumed as a preservative for both animal feed and food for human consumption. For animal feed, it is used either directly or as its ammonium salt. Another major application is as a preservative in baked goods, which use the sodium and calcium salts [16]. As a food additive, it is approved for use in the EU [17], USA [18], Australia and New Zealand [19]. Propionic acid is also useful as an intermediate in the production of other chemicals, especially thermoplastic polymers in plastic industry such as textile and rubber auxiliaries. In more specialized applications, it is also used to make pesticides and pharmaceuticals. Sometimes also used as artificial flavorings agent, dye intermediates and cosmetics.

Figure 2.3 Uses of propionic acid

2.4 Reaction

For producing propionic acid from propionaldehyde, this is the method that will be used in this study. By hydration of aldehyde, then followed by dehydrogenation as shown in Scheme 2.2. Water may be introduced into the molecule of aldehydes via hydration of aldehyde in the presence of an acid, adds rapidly to the carbonyl function of aldehydes to form hydrates known as geminal-diol or gem-diol that are unstable but that may be important intermediates in the formation of carboxylic acids by subsequent dehydrogenation.



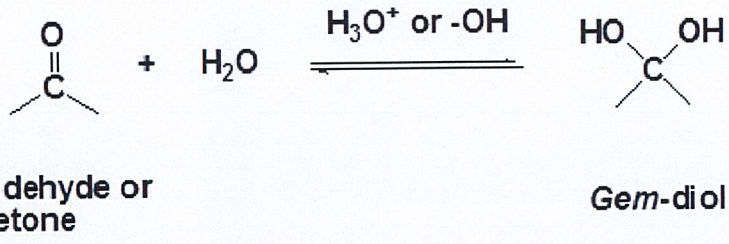
Scheme 2.2 Reaction pathway of aldehyde to carboxylic acid [20]

Oxidation reactions in the body are commonly performed in this manner, i.e. by the addition of water at a double bond followed by removal of H_2 atoms.

2.4.1 Hydration of aldehyde

Most of information about hydration relates to solutions in water. Addition of water to the carbonyl group is a reaction of some importance in organic chemistry [21] and biochemistry [22]. Thue simplest real example of this reaction is the uncatalyzed addition of water to formaldehyde in water solvent, to form methanediol [23] and aqueous solutions of acetaldehyde also have been wildly investigated [24].

It has been demonstrated in Scheme 2.3 that water, in the presence of an acid or a base, adds rapidly to the carbonyl function of aldehydes and ketones establishing a reversible equilibrium with a hydrate or germinal-diol.



Scheme 2.3 Addition of Water to form Hydrates [25]

In general, hydrates are not stable enough to be isolated as the equilibrium shifts back to starting materials. Removal of the water during a reaction can cause the conversion of a gem-diol back to the corresponding carbonyl.

Understanding the mechanism is useful before looking at the very closely related reactions of aldehyde. The mechanism is catalyzed by the addition of an acid that will be used in this study. Acidic conditions speed up the reaction because the protonated carbonyl is more electrophilic. In principle; proceed by protonation of the carbonyl (a), to reach the carbonyl carbon attack by water molecule (b) and then deprotonation to complete the formation of a gem-diol (c) is represented in Figure 2.4.

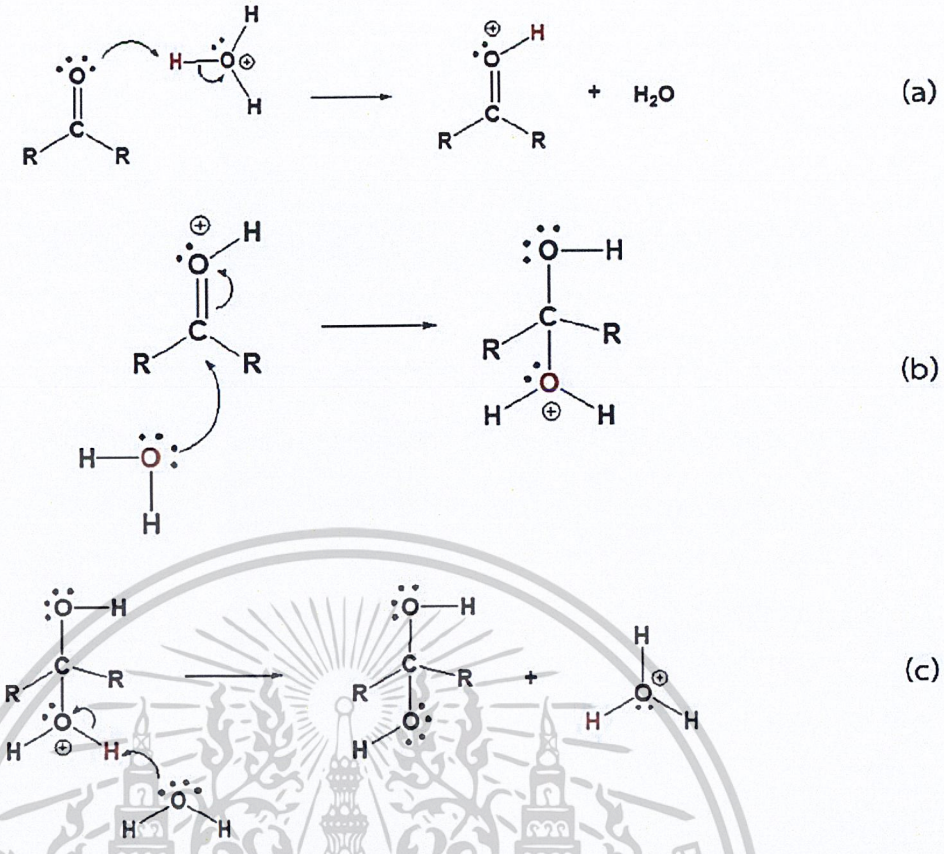
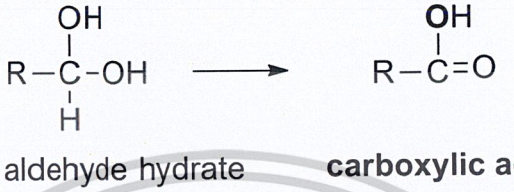


Figure 2.4 Mechanism of gem-diol formation (a) protonation (b) carbonyl carbon attack by water (c) deprotonation [25]

2.4.2 Catalytic dehydrogenation reaction

Dehydrogenation is a chemical reaction that involves the removal of hydrogen from a molecule. It is the reverse process of hydrogenation. Dehydrogenation is an endothermic reaction. Catalytic dehydrogenation can be carried out in the presence of a suitable catalyst as well as on transition metal catalysts, such as platinum, palladium or nickel. In fact, catalytic dehydrogenation typically found in a number of important industrial applications, such as employed in the production of propylene and isobutylene from propane and isobutane, in the production of C_6 to C_{19} mono-olefins from the corresponding normal alkanes and of styrene from ethylbenzene [26].

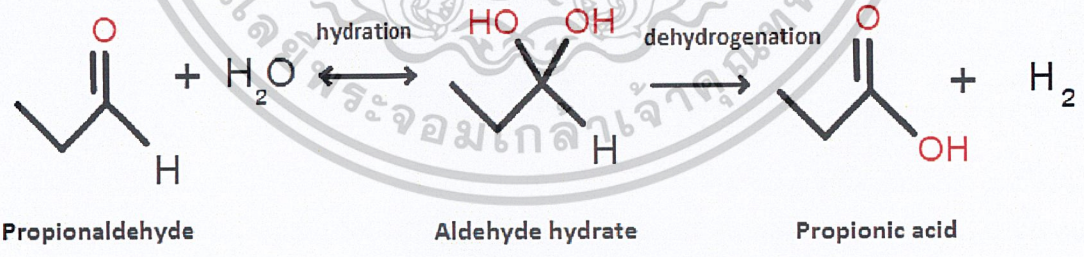
In this contribution, aldehyde hydrate (gem-diol) are usually easily dehydrogenated to the corresponding carboxylic acid over nickel catalysts, which can be represented by the expression shown in Scheme 2.4. The rates of dehydrogenation of compounds depend on the nature of catalyst, the structure of compounds, and the reaction conditions. The chemistry involved in these reactions will be discussed, with particular emphasis on the effects of catalyst.



Scheme 2.4 Dehydrogenation of hydrate to form carboxylic acid

2.4.3 Propionaldehyde to propanoic acid over Ni/SiO_2 catalysts

In this study, propionic acid can be produced from propionaldehyde by pathway as detailed above. Initially, hydration reaction, propionaldehyde react with water in the presented of acid catalyst as a silica supported to form aldehyde hydrate. Subsequently, dehydronation reaction, aldehyde hydrate rapidly dehydrogenates to propanoic acid over nickel catalyst and also yields hydrogen as a byproduct.



Scheme 2.5 Pathway of propionaldehyde to propanoic acid

2.4.4 Reaction condition

The successful performance of a hydration and catalytic dehydrogenation depends on a suitable choice of reaction conditions, in particular, the choice of catalyst, its amount and temperature.

Dehydrogenation catalysts are also subject to deactivation or promotion by various substances that are referred to as inhibitory (or poisons) or promoters, respectively. In some case, the impurities of the substrate to be dehydrogenated or the product may become a factor that retards the dehydrogenation, usually in a later stage of the reaction.

Use of elevated temperatures is usually favorable for increasing the rates of dehydrogenation that is type of endothermic reaction, dehydrogenations that proceed only slowly or not at all at a low temperature may be achieved successfully merely by raising the temperature. However, temperature increase generally causes a decrease in the efficiency and effectiveness of adsorption on silica surface [27]. This has been attributed to decrease interaction between silica surface and water as the hydrophilic group in hydration reaction. Hence, the optimum temperature that suitable for this reaction condition will be studied.

The effect of hydrogen pressure and rate of hydrogenation may depend on various factors, such as the catalyst, the substrate, the reaction conditions, etc. In most hydrogenations, however, increasing the hydrogen pressure is undoubtedly favorable for increasing the rate, reducing the reaction time, and an efficient use of catalyst.

CHAPTER 3

EXPERIMENTAL

3.1 Chemical reagents

Chemical reagents	Grade of purity	Manufacturers
1. Nickel(II) nitrate hexahydrate	99%	CARLO ERBA
2. Silicon dioxide	99.0% on dry	CARLO ERBA
3. 1-Propionaldehde	97%	ACROS
4. Distillation water		

3.2 Apparatus and instruments

1. Catalytic testing rig
2. Gas chromatograph (3800 VARIAN)
3. Laboratory glassware
4. Laboratory plastic ware
5. Oven
6. Sieve
7. Syringe (10 mL) ann Syringe pump
8. Mass flow controller
9. Tube furnace with a programmable temperature controller
10. Temperature programmed reduction (TPR) system
11. Temperature programmed desorption (TPD) system
12. Transmission electron microscopy (TEM)
13. Thermal gravimetric analysis (TGA)
14. Inductively coupled plasma mass spectrometry (ICP-MS)

3.3 Catalyst Preparation and modification

3.3.1 Preparation of silica (SiO_2) Support

A powder of SiO_2 was calcined in the tube furnace with programmable temperature controller at 500°C for 5 hour in order to get rid of moisture and excessive silanol from the silica surface.

3.3.2 Preparation of 5 wt. % Ni supported silica (SiO_2) catalysts

Before impregnation, the supports were dried at 80°C in an oven for 24 hour in order to remove moisture and impurity.

The 0.2 M Ni precursor solution was prepared by dissolving 2.5000 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 41 mL of water. After that, 9.5000 g of SiO_2 was impregnated with the Ni precursor solution in plastic beaker. The mixture was gradually dried in an oven at 100°C overnight to remove excess water till support is almost dry. Then, it was calcined in a tube furnace at 5°C/min to 500°C for 5 hour to obtain NiO. After that, NiO was reduced at 10°C/min to 450°C for 3 hour under the steam of hydrogen pressure (100 mL/min) in a reactor to obtain Ni metal form.

3.3.3 Preparation of 20 wt. % Ni supported silica (SiO_2) catalysts

The 1 M Ni precursor solution was prepared by dissolving 10.0100 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 35 mL of water. After that, 8.0000 g of SiO_2 was impregnated with the Ni precursor solution in plastic beaker. Then, Ni supported on SiO_2 catalyst was also prepared by using the same procedure described above.

3.4 Characterization of catalysts

3.4.1 Temperature programmed reduction (TPR)

Temperature-programmed reduction (TPR) provides information on the active site species of the catalysts by monitoring their reducibility. Temperature programmed reduction was measured using thermal conductivity detector (TCD). The sample weighed 0.1 g was placed into a quartz tube reactor, which was located inside a temperature-regulated furnace. Prior to the H_2-TPR, each sample was heated to its calcinations temperature in air zero for 1 h (15 mL/min) and cooled to 50°C. The heating rate of 2°C/min, the 5% H_2 in He flow of 25 mL/min was applied for TPR

analysis. Water produced during the reduction process will be removed in a U-shape glass trap at -70°C (vapor of liquid N_2) before entering the TCD.

3.5 Catalytic Activity testing

3.5.1 Reaction of propionaldehyde to propionic acid

The Ni supported on silica catalyst pellets were packed into the glass reactor (8 mm of inside diameter) and covered by glass wool. The glass beads were loaded under the catalysts bed to facilitate feed flow dispersion.

The catalytic testing rig is shown in Figure 3.1. The reactor was positioned at the center of a vertical tube furnace. The gas flows will be controlled by mass flow controllers and checked by bubble flow meter. The catalysts were activated by heating at 5°C/min to 500°C and held at that temperature for 1 hour under the steam of air zero (60 mL/min). After that, the reactor was cooled down to the reaction temperature. To start the reaction, 5 wt. % of propionaldehyde solution was fed into the reactor by syringe pump at 0.75 g/h. The reaction was operated for 6 hour on steam and the product effluents will be collected hourly.

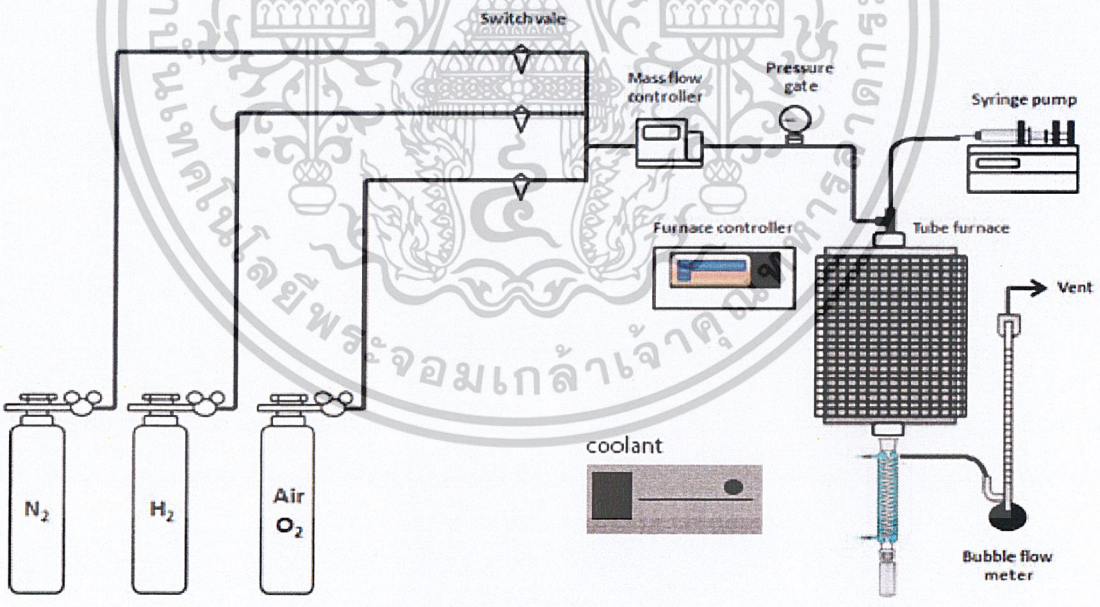


Figure 3.1 The schematic diagram of the catalytic testing rig

The description of the reaction set up and the reaction condition are summarized in Table 3.1

Table 3.1 Description of the reactor set up and the reaction conditions

Parameters	Value
Reactor inside diameter (mm)	6
Reactor outside diameter (mm)	8
Total flow (mL/min)	60
Bed length (cm)	25
Contact time: W/F (g.h/mol)	250-500
Catalyst activation (before reaction)	Heating rate: 5°C/min
	Heat treatment: 500°C hold for 1 hours
	Gas: air zero (60 mL/min)
Carrier gas	H_2
Reaction temperature	165-220°C
Total reaction pressure	Atmospheric pressure

3.6 Products analysis

Products were carried out through the fix-bed reactor periodically and analyzed by gas chromatography (GC) equipped with flame ionized detector (GC-FID Varian CP-3800). FFAP (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm) was used as a separating column. The following temperature program; linear velocity is 23.5 cm/sec, 60°C hold for 2 min, then ramp at 8°C/min to 200°C hold at this temperature for 5.5 min by using N_2 as a carrier gas.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 Temperature Program Reduction Characteristics

To investigate the interaction between nickel oxide and silica, temperature programmed reduction (H_2-TPR) was carried out with catalysts of different Ni contents (5%, 10%, 15% and 20% wt. Ni/SiO_2 catalyst). The H_2-TPR profile of those catalysts prepared by impregnation method is shown in Figure 4.1.

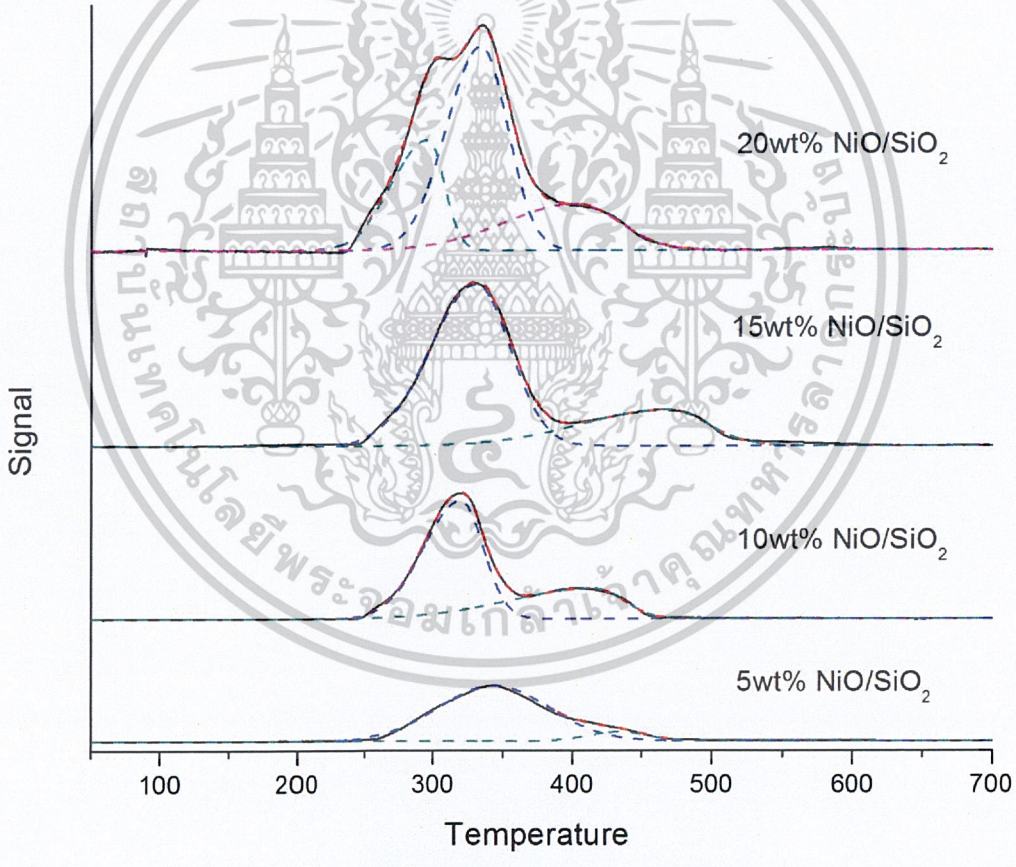


Figure 4.1 TPR profiles of 5% wt., 10% wt., 15% wt. and 20% wt. Ni/SiO_2 catalysts

As seen from Figure 4.1, the reduction of 5%, 10% and 15% wt. NiO/SiO_2 to metallic Nickel (Ni^0) exhibit two peaks. All samples show the first H_2 consumption

peak at 340°C and another broad peak at 420°C, 430°C and 450°C for 5%, 10% and 15% wt. NiO/SiO_2, respectively. For 20% wt. NiO/SiO_2 catalyst, three reduction peaks at 300°C, 340°C and 420°C can be observed.

The peak at 340°C is ascribed to the reduction of aggregated NiO on the surface to metallic Ni [35], while broad peak at higher temperature can be referred to the reduction of nickel silicate species [46]. Furthermore, the reduction peak area at 340°C increases with nickel loadings, but the broad peak is increased only slightly. This suggests that the additional nickel tends to form NiO on silica surface. Similar observation was reported by B. Bej for nickel catalyst supported on silica [34].

For 20% wt. NiO/SiO_2 catalyst, both of the reduction peaks at 300°C and 340°C is also ascribed to the reduction of the aggregated NiO on the surface to metallic Ni. However, the reduction peak at 300°C is lower of H_2 consumption than the peak at 340°C. This can be explained by the different particle size of the NiO aggregates. The larger NiO particle size is reduced at higher temperature (340°C), while the smaller one can be easily reduced at lower temperature (300°C).

4.2 Catalytic testing

4.2.1 Reaction of propionaldehyde to propionic acid

The conversions of propionaldehyde to propionic acid via water reduction were tested by varying contact time, reaction temperature, reduction temperature and Ni loadings.

4.2.1.1 Effect of contact time

In order to understand the reaction pathway for the conversion of propionaldehyde to propionic acid, 20% wt. Ni/SiO_2 catalyst was tested at various contact times at 195°C. The results are shown in Figure 4.2.

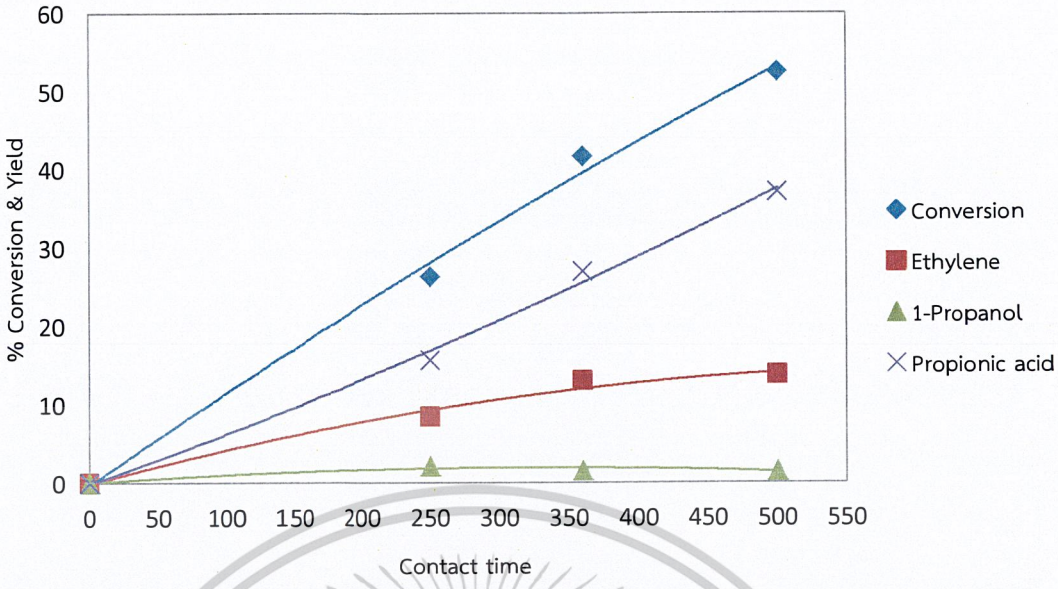
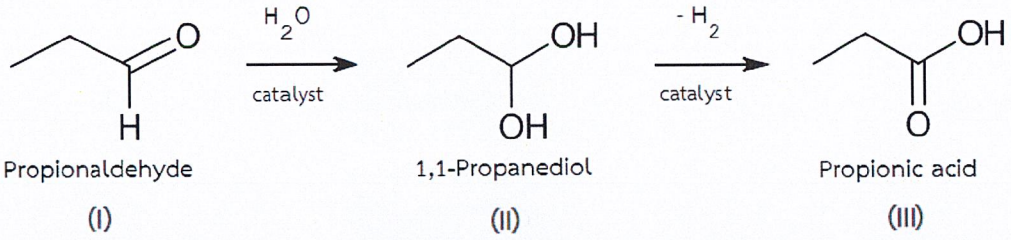


Figure 4.2 The conversion and products yield as a function of contact time

Reaction conditions; temperature: 195°C, feed: 0.795 g/h of 5% wt. propionaldehyde, catalyst: 20% wt. Ni/SiO_2, ambient pressure, 60 mL/min of nitrogen

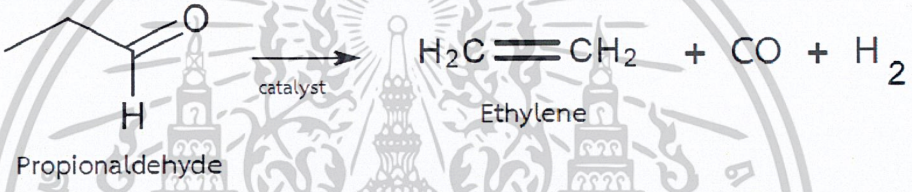
According to Figure 4.2, propionaldehyde conversion is significantly improved by increasing the contact time from 250 g.h/mol (26.39%) to 360 g.h/mol (41.76%) and 500 g.h/mol (52.50%). Propionic acid is found as a major product; while, ethylene and 1-propanol are also found as a minor products.

Propionic acid can be formed by water reduction. Since water is largely present in the reaction, it may react with propionaldehyde (i). The hydration typically takes places at the carbonyl group of aldehydes to form hydrates known as geminal-diol [25]. The hydrated product from propionaldehyde is 1,1-propanediol (ii), that can be easily dehydrogenated over Ni surface to propionic acid (iii). The formation of propionic acid indicates that H_2 must be formed by reaction of propionaldehyde and water i.e. water reduction as shown in Scheme 4.1



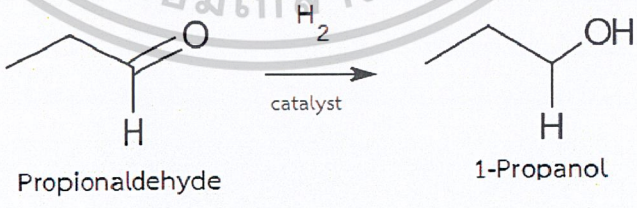
Scheme 4.1 The propionic acid formation

From Figure 4.2, ethylene and 1-propanol are also found in parallel as minor products. Ethylene is formed by the decarbonylation of propionaldehyde on Ni surface, bearing carbon monoxide (CO) and hydrogen (H_2) [30] as co-products. (Scheme 4.2)



Scheme 4.2 The decarbonylation of propionaldehyde to ethylene

1-Propanol can be produced from hydrogenation of propionaldehyde at carbonyl group [29]. As H_2 gas is largely produced from water reduction (Scheme 4.1) and decarbonylation (Scheme 4.2), the observed 1-propanol as co-product is further evidence for H_2 production from the reaction of propionaldehyde and water. The hydrogenation of propionaldehyde to 1-propanol is shown in Scheme 4.3.



Scheme 4.3 The hydrogenation of propionaldehyde to 1-propanol

The selectivity of all products as a function of contact time is shown in Figure 4.3.

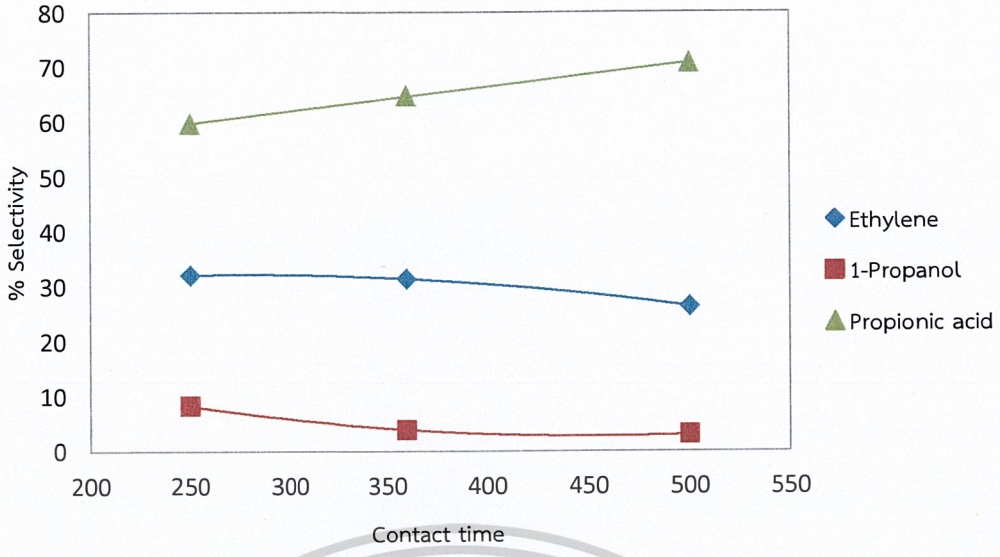
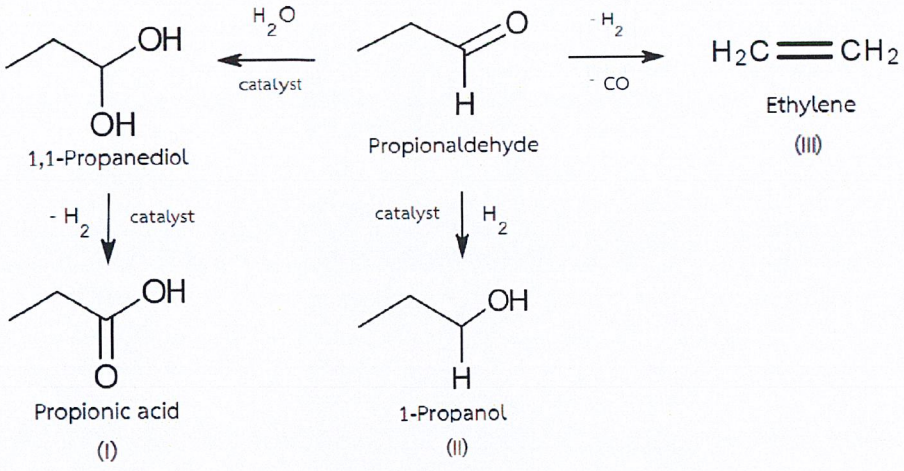


Figure 4.3 The selectivity of propionaldehyde to ethylene, 1-propanol and propionic acid as a function of contact time

Reaction conditions; temperature: 195°C, feed: 0.795 g/h of 5% wt. propionaldehyde, catalyst: 20% wt. Ni/SiO_2, ambient pressure, 60 mL/min of nitrogen

According to Figure 4.3, when contact time is increased, the selectivity to all products remains in the same range. However, the selectivity to propionic acid is slightly increased while the selectivity to ethylene and 1-propanol is slightly decreased. This suggests that at longer contact time, the reaction rate of water reduction is greater than decarbonylation and hydrogenation.

The overall reaction pathway of propionaldehyde can be summarized as shown below in Scheme 4.4.



Scheme 4.4 The overall reaction pathway of propionaldehyde

4.2.1.2 Effect of reaction temperatures

The effect of reaction temperature of propionic acid from propionaldehyde over 20% wt. Ni/SiO_2 was investigated. The results are shown in Figure 4.4.

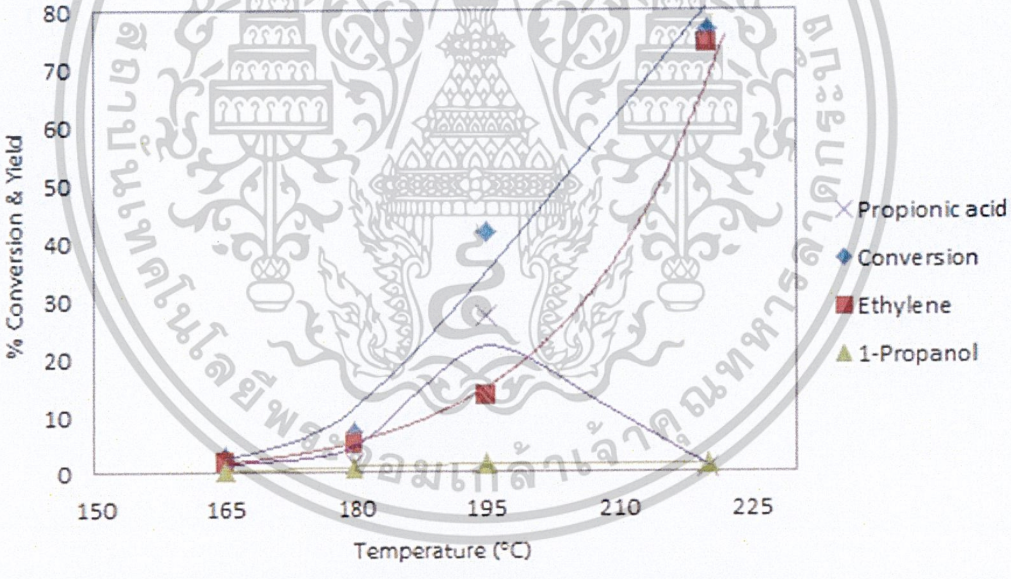


Figure 4.4 The effect of reaction temperature for propionaldehyde conversion and yield

Reaction condition; temperature: 165-220°C, ambient pressure, contact time: 360 g.h/mol, catalyst: 20% wt. Ni/SiO_2, feed: 0.795 g/h of 5% wt. Propionaldehyde, carrier gas: 60 mL/min N_2

The results show that as the temperature is increased, the conversion is also increased from 165°C (2.87%), 180°C (7.08%), 195°C (41.76%) and 220°C (76.60%). This can be explained that changing the temperature affects the rate of a reaction. As the temperature is increased the rate of reaction is also increased.

The yield of propionic acid is negligibly obtained at 165°C (0.55%) and 180°C (1.47%). This suggests that the temperature maybe not high enough for 1,1-propanediol to be further dehydrogenated to propionic acid. This is because the dehydrogenation is endothermic and usually takes place at high temperature [26]. However, propionic acid can be found at 195°C (27.05%). It could imply that the dehydrogenation of 1,1-propanediol can be promoted at this temperature. However, propionic acid yield is suddenly dropped at 220°C (0.93%). This is because the temperature is too high for the hydration of propionaldehyde (Scheme 4.1). The hydration reaction is favorable at low temperature because it is an exothermic reaction [30]. Moreover, as the temperature is decreased the adsorption capacity is also increased. Therefore, the optimum temperature for production of propionic acid is a balance between hydration and dehydrogenation.

For ethylene, the yield of ethylene at 165°C (2.00%), 180°C (4.87%) are higher than yield of propionic acid. This can be explained as mentioned previously that 1,1-propanediol maybe form on SiO_2 surface, but cannot be further dehydrogenated to propionic acid at low temperature. In parallel, the propionaldehyde can be decarbonylated to ethylene instead. As the temperature is increased, the decarbonylation of propionaldehyde is promoted particularly at 220°C (74.31%). Hence, only ethylene can be observed at high temperature.

The yield of 1-propanol still remained very low even increasing temperature. Because the hydrogenation of propionaldehyde to 1-propanol is usually required to facilitate the reaction at lower temperature [33]. Hence, the yield of 1-propanol is not improved by increasing temperature.

The selectivity of products are varied with temperature, as shown in Figure 4.5

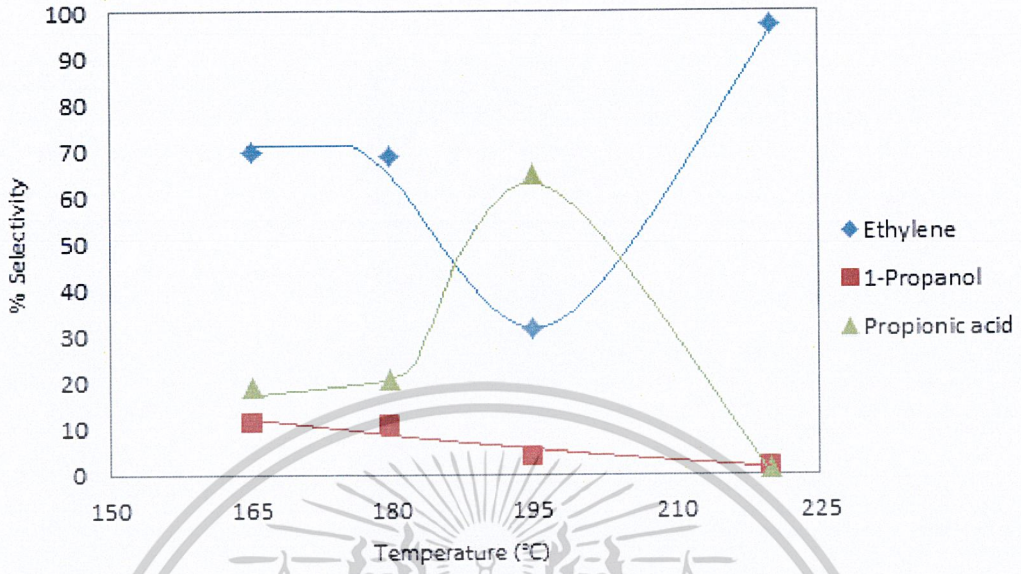


Figure 4.5 The selectivity of propionaldehyde to ethylene, 1-propanol and propionic acid as a function of reaction temperature

Reaction condition; temperature: 165-220°C, ambient pressure, contact time: 360 g.h/mol, catalyst: 20% wt. Ni/SiO_2, feed: 0.795 g/h of 5% wt. Propionaldehyde, carrier gas: nitrogen at 60 mL/min

From Figure 4.5, it can be seen that the optimum temperature for production of propionic acid is at 195°C, in this study. This is because at the lower temperature, 1,1-propanediol cannot be dehydrogenated to propionic acid. Moreover at higher temperature (220°C), the decarbonylation of propionaldehyde is promoted and ethylene is observed instead of propionic acid.

4.2.1.3 Effect of Ni loadings (% wt.)

The water reduction of propionaldehyde over different Ni loadings (% wt.) supported on silica catalysts was carried out at 195°C, contact time of 500 g.h/mol and ambient pressure. The results are given in Figure 4.6.

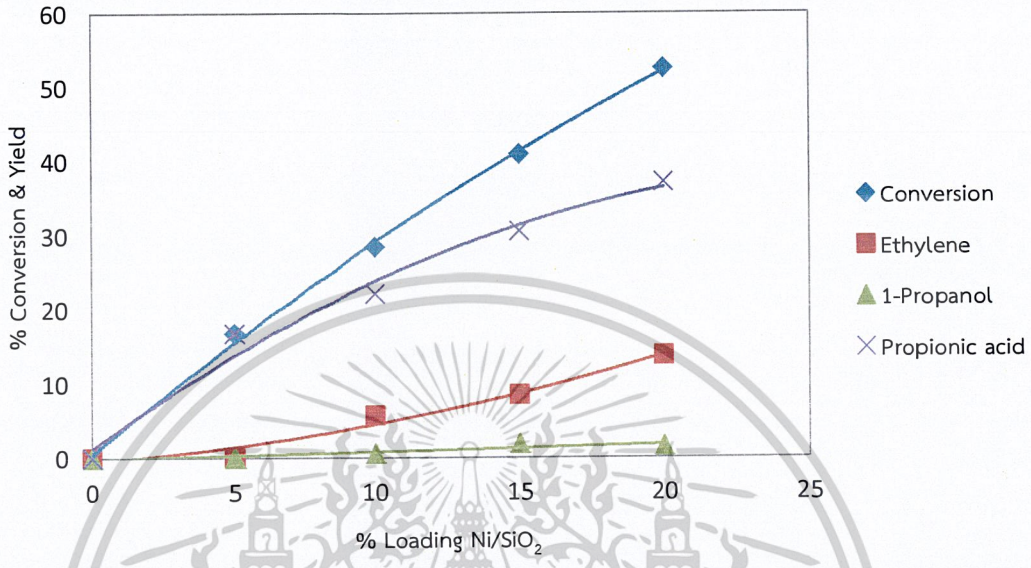


Figure 4.6 The conversion and yield as a function of loading Ni/SiO_2 (% wt.)

Reaction condition; temperature: 195°C, contact time: 500 g.h/mol, ambient pressure, feed: 0.795 g/h Propionaldehyde of 5% wt., 60 mL/min nitrogen

The results show that the conversion of propionaldehyde is improved as the nickel loading (% wt.) is increased. Conversion of propionaldehyde over 5% wt., 10% wt., 15% wt. and 20% wt. Ni/SiO_2 are 16.84%, 28.53%, 40.96% and 52.50%, respectively. As nickel loading (% wt.) is increased, the overall interaction of reactant with the proportionally Ni active sites is enhanced. Hence, conversion is promoted by increasing nickel loading.

The selectivity of products are varied with the nickel loading (% wt.), as shown in Figure 4.7.

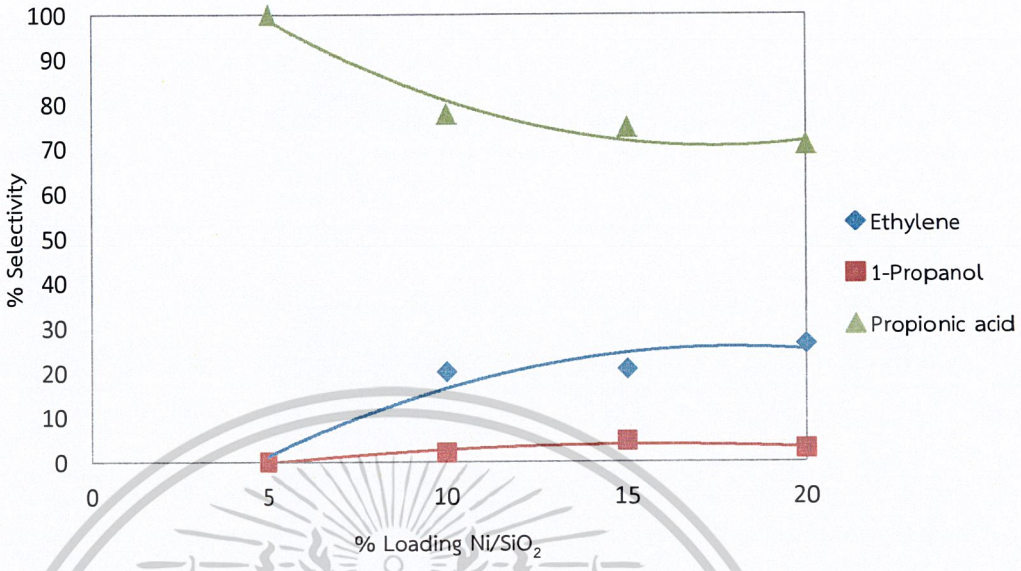


Figure 4.7 The selectivity of propionaldehyde to ethylene, 1-propanol and propionic acid as a function of loading Ni/SiO_2 (% wt.)

Reaction condition; temperature: 195°C, contact time: 500 g.h/mol, ambient pressure, feed: 0.795 g/h Propionaldehyde of 5% wt., 60 mL/min nitrogen

The 10% wt., 15% wt., and 20% wt. Ni/SiO_2 catalysts exhibit a similar selectivity of all products while, the 5% wt. Ni/SiO_2 catalyst provides high selectivity to propionic acid (100.0%).

This can be explained that low metal loading (i.e. 5% wt. Ni/SiO_2) catalysts typically have small particle sizes. While, the high metal loading catalysts (i.e. 10%, 15%, and 20% wt. Ni/SiO_2) have large particle sizes. As the appropriate adsorption mode is required for particular reaction, the particle size would affect the selectivity. For example, the water reduction process requires only the carbonyl group of propionaldehyde on the surface of Ni metal (a), while the decarbonylation need both carbonyl group and carbon on the metal surface (b), as demonstrated in Figure 4.8

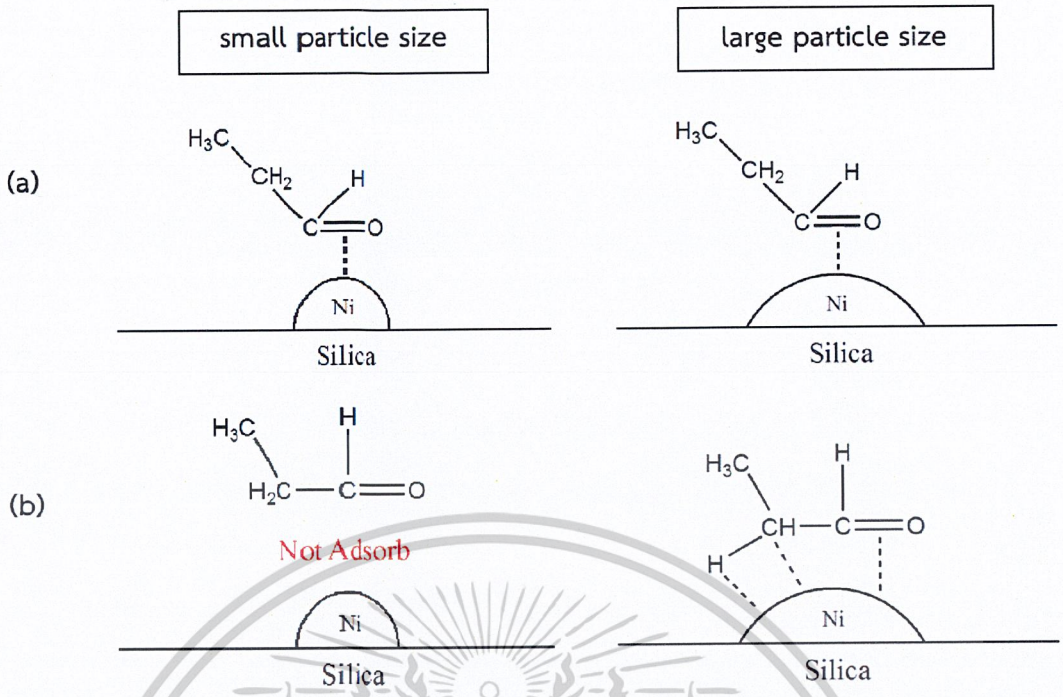


Figure 4.8 Propionaldehyde on Ni metal catalyst surface; (a) for the water reduction and (b) for the decarbonylation

From Figure 4.8, it is noticed that three atoms (carbon and carbonyl group) of propionaldehyde can adsorb only on the large Ni ensemble. Nickel with small particle size cannot accommodate such adsorption. Hence, the decarbonylation of propionaldehyde to ethylene is only promoted over the catalyst with large particle size (high nickel loadings). While, the carbonyl group can adsorb on both small and large Ni particle. Hence, propionaldehyde is converted to propionic acid as a main product for all loadings. This is particularly the case for the small particle catalyst (5% wt. Ni/SiO_2) with high Ni/SiO_2 interface where water can readily interact with the adsorb propionaldehyde on Ni particle as shown in Figure 4.9

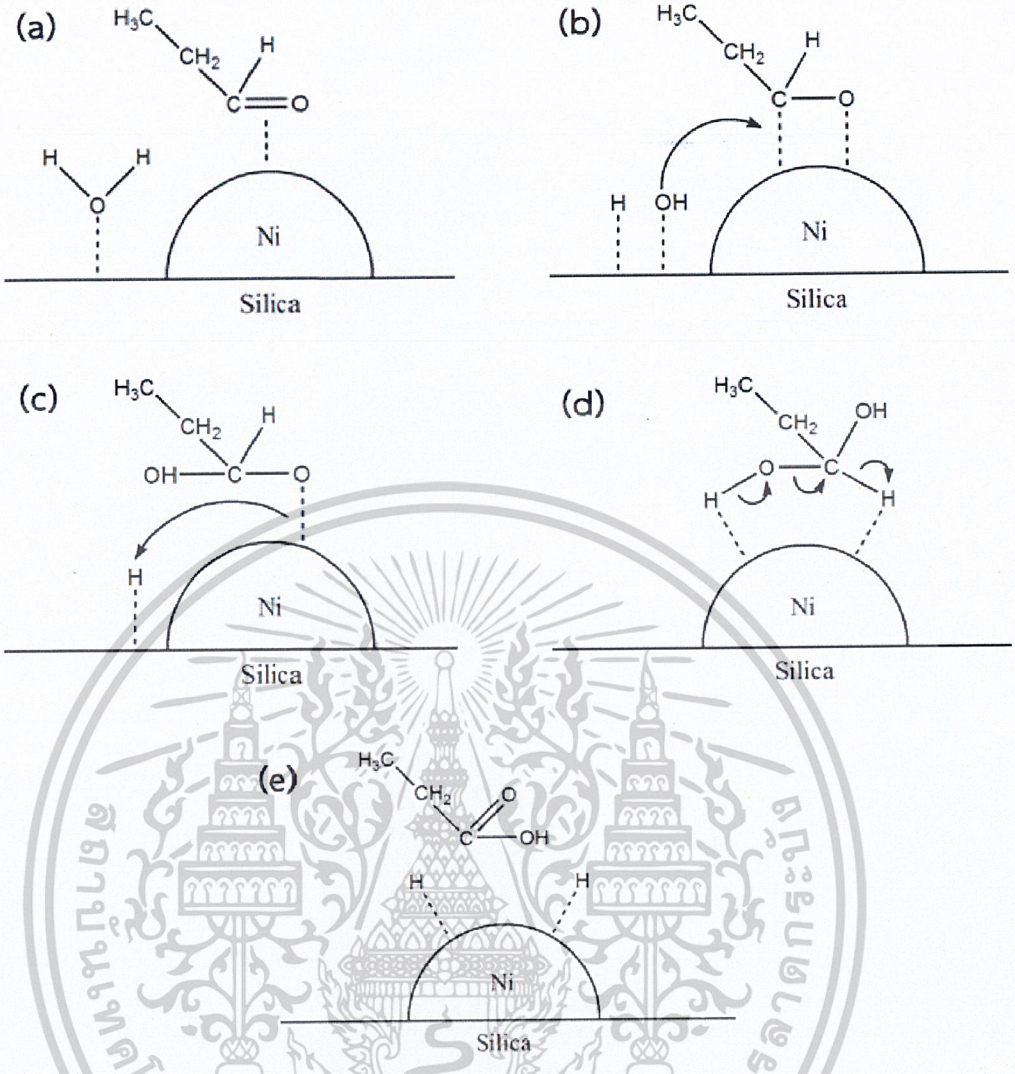


Figure 4.9 The water reduction on catalyst surface

From Figure 4.9, it can be seen that the water adsorption takes place at the surface of silica. While, propionaldehyde adsorb on the surface of nickel (a). The small Ni particle would provide high Ni/SiO_2 interface and interaction between propionaldehyde and water (b) to form 1,1-propanediol (c-d), a precursor for propionic acid (e).

4.2.1.4 Effect of reduction temperature

The effect of reduction temperature of propionaldehyde to propionic acid over 10% wt. Ni/SiO_2 at reduction temperature of 360°C and 450°C were investigated. The results are shown in Figure 4.10.

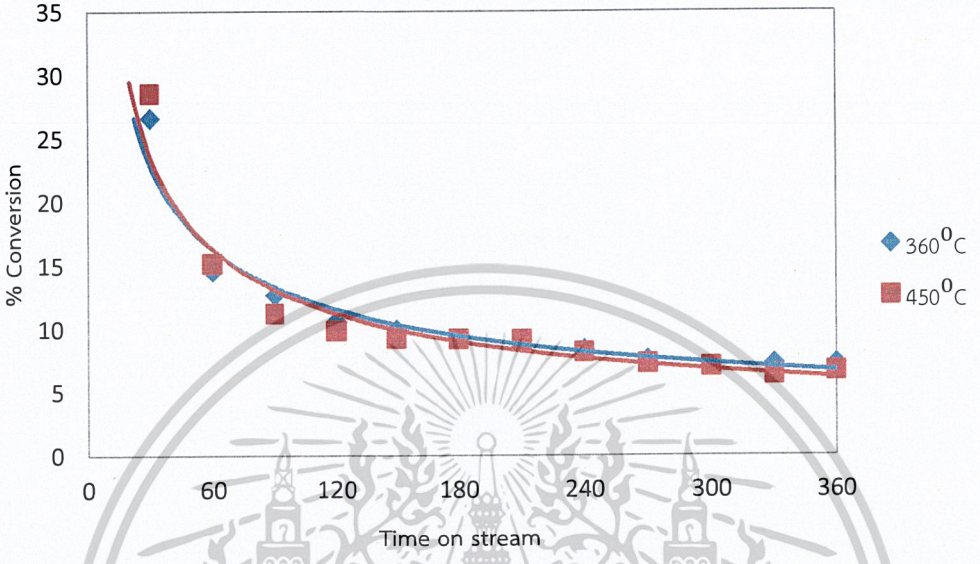


Figure 4.10 Effect of reduction temperature at 360°C and 450°C

Reaction condition; reaction temperature: 195°C, contact time: 500 g.h/mol, catalyst: 10% wt. Ni/SiO_2, ambient pressure, feed: 0.795 g/h propionaldehyde of 5% wt., 60 mL/min nitrogen

From Figure 4.10, the results show that the reduction temperature at both 360°C and 450°C exhibit a similar conversion of propionaldehyde and products selectivity as shown in table 4.1.

Table 4.1 Products selectivity obtained from propionaldehyde conversion

Reduction Temperature	Selectivity		
	Ethylene	1-Propanol	Propionic acid
360°C	24.92	2.37	72.71
450°C	20.17	2.06	77.76

As shown by H_2-TPR of NiO catalyst (Figure 4.1), only NiO species can be reduced to metallic Ni at 360°C. While, both NiO and nickel silicate species can be

reduced at 450°C. However, the conversion of propionaldehyde is similar for both catalysts reduce at 360°C and 450°C. Therefore, the observed activity would be derived from the reduction of NiO species and nickel silicate species plays no role in the water reduction.

This is because nickel silicate species cannot be reduced to form nickel metal on the surface as demonstrated by the second H_2-temperature programmed reduction (H_2-TPR) in Figure 4.11.

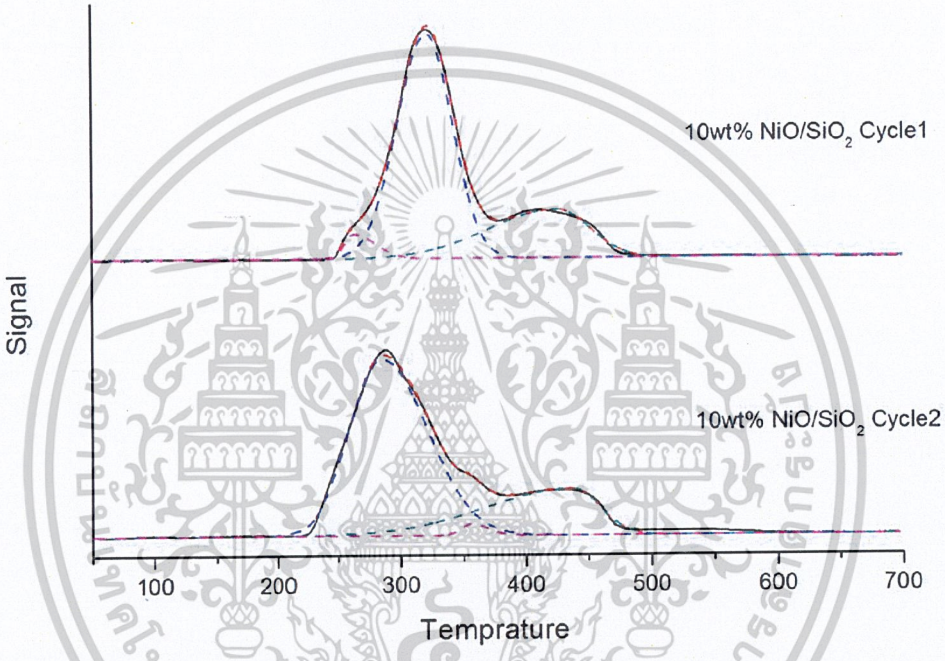


Figure 4.11 The secondary H_2-TPR profiles of 10% wt. Ni/SiO_2 catalyst

From Figure 4.11, after the primary H_2-TPR was proceeding, the catalyst was then cooled down by N_2 to 500°C and hold for 1 hour to re-oxidize in air zero. After that, cooled to 50°C by purging in N_2 and the secondary H_2-TPR cycle was repeated as the same condition again. It was found that both the primary and secondary H_2-TPR cycles exhibit similar results. However, the first H_2 consumption (320°C) is shifted to a lower temperature (290°C). This suggests that the particle size of aggregated NiO formed after re-oxidation is smaller than that obtained by initial impregnation. In other words, purging O_2 at 500°C after the primary H_2-TPR can re-disperse NiO on the surface. Hence, it can be easily reduced at lower temperature during the secondary H_2-TPR. However, the reduction of nickel silicate species (broad peak ~ 420°C) remains the same. Therefore, it can be summarized that no additional Ni metal on

the surface can be formed from nickel silicate species after reduction. It is likely that reduction of nickel silicate (420°C) yields encapsulated Ni metal in the silica matrix.

4.2.1.5 Catalytic deactivation

From the previous result, all catalysts seem to show deactivation. Accordingly, the effect of time on stream at reaction temperature of 195°C for the conversion of propionaldehyde to propionic acid over 5%, 10%, 15% and 20% wt. Ni/SiO_2 catalyst are studied as shown in Figure 4.12.

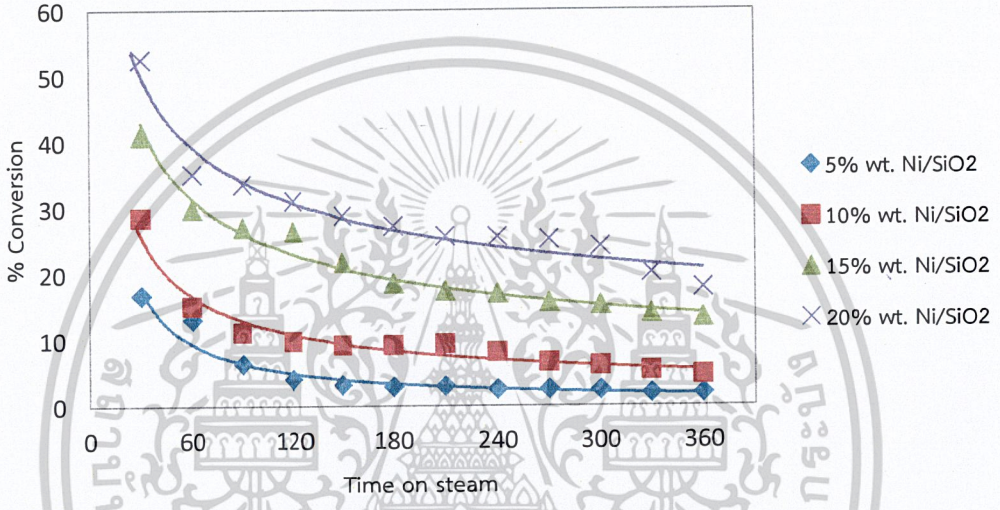


Figure 4.12 Conversion of propionaldehyde over Ni/SiO_2 with difference loading as a function of time on stream

Reaction condition; temperature: 195°C, contact time: 500 g.h/mol, catalyst: 20% wt. Ni/SiO_2, ambient pressure, feed: 0.795 g/h propionaldehyde of 5% wt., 60 mL/min nitrogen

From Figure 4.12, the conversion of propionaldehyde over all loadings of Ni/SiO_2 catalysts is decreased with time on steam; all loadings of Ni/SiO_2 catalysts show deactivation in a similar manner.

The catalyst deactivation is possible due to (i) leaching of metal function, (ii) sintering of metal, (iii) strong adsorption of reactant and product or (iv) deposition of high molecular weight product over catalyst. It has been proven in a previous work [4] that higher molecular weight species or coke are deposited on the surface of the Ni/SiO_2 catalysts, leading to a significant decrease in propionic acid yield over time on stream [4].

CHAPTER 5
CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The water reduction of propionaldehyde to propionic acid and hydrogen was studied over Ni/SiO_2 catalyst. Hydration at the carbonyl group of propionaldehyde results in 1,1-propanediol that can be easily dehydrogenated over Ni surface to propionic acid. The formation of propionic acid indicates that H_2 must be formed via the dehydrogenation process. However, ethylene and 1-propanol are also obtained in parallel. Ethylene is formed by decarbonylation of propionaldehyde, particularly over the catalyst with large particle size (i.e. high nickel loading) and at high temperature (>195°C). 1-Propanol can be produced from hydrogenation of propionaldehyde with H_2, largely produced from the water reduction and the decarbonylation processes.

As the temperature is increased, rate of the reaction is increased. However, product selectivity was modified by temperature. The optimum temperature for the water reduction (to obtain propionic acid and hydrogen) is at 195°C. At the lower temperature (i.e. 165°C and 180°C) 1,1-propanediol cannot be dehydrogenated to propionic acid and hydrogen. While, at the higher temperature (i.e. 220°C), the decarbonylation of propionaldehyde is competitively promoted to form ethylene.

As nickel loading is increased, the overall interaction of propionaldehyde with the Ni metal surface is enhanced and hence, the conversion can be promoted. Moreover, the results show that the catalyst with high Ni loadings (i.e. 10%, 15%, and 20% wt. Ni/SiO_2) possess large Ni particle size, and give a similar products selectivity. While, the catalyst with low Ni loading (i.e. 5% wt. Ni/SiO_2) retains small particle size, and provides high selectivity to propionic acid and hydrogen (100%). This is because the decarbonylation requires complex multinuclear adsorption of propionaldehyde on the large Ni particle. While, the water reduction can be promoted via mononuclear adsorption of propionaldehyde, particularly on the small Ni particle. This is due to a high

$Ni\text{-}SiO_2$ interface where the water adsorbed on silica, can readily interact with the adsorbed propionaldehyde on Ni metal particle.

The reduction temperature at both 360°C and 450°C exhibit a similar propionaldehyde conversion and products selectivity. This is because the observed activity and selectivity would be derived only from the Ni metal on the surface. The reduction of nickel silicate species yields encapsulated Ni metal in the silica matrix. Hence, the nickel silicate species provides no activity for the observed conversion.

5.2 Suggestions for Future Studies

5.2.1 Hydrogen product from the water reduction process could be stored for the advancement of hydrogen and technologies in applications.

5.2.2 Changing supported catalysts are interested to increase activity and selectivity of propionaldehyde to propionic acid and hydrogen.

REFERENCES

1. Alberto Villa, Sebastiano Campisi, Khaled M. H. Mohammed, Nikolaos Dimitratos, Floriana Vindigni, Maela Manzoli, Wilm Jones, Michael Bowker, Graham J. Hutchings and Laura Prati. "Tailoring the selectivity of glycerol oxidation by tuning the acid–base properties of Au catalysts." *Catalysis Science & Technology* 5 (2015) 1126-1132.
2. L. Znak, J. Zielin´ski. "Effects of support on hydrogen adsorption/desorption on nickel." *Applied Catalysis A: General* 334 (2008) 268–276.
3. Laura, Malek. 2012. **Simulation of propionaldehyde production from glycerol.** Sweden: Chemical Engineering.
4. K. Matee, C. Homlaor and P. Duangchan. 2014. **Catalytic deoxygenation of glycerol to 1-propanol over zeolite and supported Ni catalysts in sequential bed system**
5. Christian Hulteberg, Jan Brandin, Richard R. Woods, Brook Porter. 2009. **Short chain alcohol production from glycerin**
6. 2013. **Propionaldehyde Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2013 - 2019.** [Online]. Available : http://www.transparencymarketresearch.com/propionaldehyde-market.html
7. S.A. Stevenson, R.T.K. Baker, J.A. Dumesic, E. Ruckenstein (Eds.), **Metal–Support Interactions in Catalysis, Sintering, and Redispersion**. Catalysis Series, Van Nostrand Reinhold, New York, 1987.
8. M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 5383.
9. M. Haruta, Catal. Today 36 (1997) 153.
10. B.K. Min, A.K. Santra and D.W. Goodman. "Understanding silica-supported metal catalysts: Pd/silica as a case study." *Catalysis Today* 85 (2003) 113–124
11. Jinzhang Gao, Fei Guan, Yanchun Zhao, Wu Yang, Yongjun Ma, Xiaoquan Lu, Jingguo Hou and Jingwan Kang. "Preparation of ultrafine nickel powder and its catalytic dehydrogenation activity" *Materials Chemistry and Physics* 71 (2001) 215–219
12. Nishimura, S. **Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis..** 1-3, 51-59, 170

13. Homzra Dkins and Howarid Cramer. "The use of nickel as a catalyst for hydrogenation." *American chemical society* 52 (1930) 4349-4358.
14. Busca, G. Heterogeneous Catalytic Materials. 131-136, 161-164, 316-320.
15. Anderson, J. A. and Garcia, M. F. **Supported Metals in Catalysis.** 71.
16. W. Bertleff; M. Roeper; X. Sava (2005), "Carbonylation", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH,doi:10.1002/14356007.a05_217
17. "Current EU approved additives and their E Numbers". UK Food Standards Agency. Retrieved 2011-10-27.
18. "Listing of Food Additives Status Part II". US Food and Drug Administration. Retrieved 2011-10-27.
19. "Standard 1.2.4 - Labelling of ingredients". Australia New Zealand Food Standards Code. Comlaw.au. Retrieved 2011-10-27.
20. **From atoms to molecules.** [Online]. Available : http://pocketdentistry.com/from-atoms-to-molecules/
21. Bell, R. P. "The Reversible Hydration of Carbonyl Compounds." *Adv. Phys. Org. Chem.* 1966, 4, 1-29.
22. Jencks, W. P. "Catalysis in Chemistry and Enzymology." Dover Publications, Inc.: New York, 1987.
23. Saul Wolfe, Chan-Kyung Kim, KiyuU Yang, Noham Weinberg and Zheng Shi. "Hydration of the Carbonyl Group. A Theoretical Study of the Cooperative Mechanism." *J. Am. Chem. SOC.* 1995,117, 4240-4260
24. R.P. Bell. The reversible hydration of carbonyl compounds. V. Gold (Ed.), **Advance in Physical and Organic Chemistry**, Vol. 4 Academic Press, New York 1966.
25. **Addition of Water to form Hydrates (Gem-Diols).** [Online]. Available : http://chemwiki.ucdavis.edu/?title=Organic_Chemistry/Aldehydes_and_Ketones/Reactivity_of_Aldehydes_%26_Ketones/Addition_of_Water_to_form_Hydrates_(Gem-Diols)
26. Daniel E. Resasco. (2000) **Dehydrogenation by Heterogeneous Catalysts.** Encyclopedia of Catalysis: School of Chemical Engineering and Materials Science University of Oklahoma
27. Milton J. Rosen. (2004) **Surfactants and Interfacial Phenomena.** Surfactant research institute: The city university of New York

28. Luis E. Murillo. (2008) **Controlling Hydrogenation Activity and Selectivity of Bimetallic Surfaces and Catalysts. The** University of Delaware : Materials Science and Engineering

29. Wang, Z. Li, G. Liu, X. Huang, Y. Wang, A. Chu, W. Wang, X. and Li, N. 2014. "Aqueous phase hydrogenation of acetic acid to ethanol over Ir-MoO_x/SiO_2 catalyst" Catalysis Communications. 43 : 38–41.

30. N. F. Brown, M. A. Barteau. "Reactions of 1-propanol and propionaldehyde on rhodium(111)" *Langmuir* 8 (1992) 862–869.

31. **"Solutions and Heats of Hydration."** Boundless Chemistry. 21 Jul 2015. Retrieved 28 Mar 2016. [Online]. Available : https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/solutions-12/properties-of-solutions-92/solutions-and-heats-of-hydration-399-4883/

32. Chinnappan Baskar, Shikha Baskar and Ranjit S. Dhillon. (2012) **Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials Science.** Department of chemistry Punjab Agriculture University

33. **"Hydrogenation."** Boundless Chemistry. Boundless, 21 Jul. 2015. Retrieved 17 Apr. 2016 [Online]. Available : https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/nonmetallic-elements-21/hydrogen-148/hydrogenation-574-6869/

34. Barnali Bej, Narayan C. Pradhan and Swati Neogi. "Production of hydrogen by steam reforming of methane over alumina supported nano-NiO/SiO_2 catalyst". *Catalysis Today* 207 (2013) 28–35

35. LIU Yingxin, CHEN Jixiang and ZHANG Jiyan. "Effects of the Supports on Activity of Supported Nickel Catalysts for Hydrogenation of *m*-Dinitrobenzene to *m*-Phenylenediamine." *Chin. J. Chem. Eng.,* 15(1) 63—67 (2007)

36. Robert L. Augustine. (1995) **Heterogeneous Catalysis for the Synthetic Chemist** Seton Hall University: Department of chemistry

37. L.T. Zhuravlev. "Colloids and Surfaces A: Physicochem". *Eng. Aspects* 173 (2000) 1–38

APPENDICES

APPENDIX A

Reaction Data

A1: Effect of Contact time

Table A1 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at contact time of 250 g.h.mol^{-1}

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	26.4	8.5	2.2	15.8
1	26.2	10.0	2.8	13.5
1.5	25.0	10.1	2.7	12.2
2	24.0	9.2	1.8	13.0
2.5	18.6	7.6	1.4	9.5
3	17.5	8.3	1.3	7.9
3.5	17.2	7.7	1.1	8.4
4	16.2	5.6	0.9	9.7
4.5	15.9	6.5	1.1	8.3
5	13.5	5.3	0.7	7.5
5.5	12.7	5.3	0.7	6.7
6	12.3	5.2	0.8	6.3

Reaction condition; temperature: 195°C, feed: 0.795 g/h of 5% wt. propionaldehyde, catalyst: 20% wt. Ni/SiO_2, ambient pressure, 60 mL/min of Nitrogen

Table A2 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at contact time of 360 g.h.mol^{-1}

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	41.8	13.1	1.6	27.0
1	34.8	14.6	5.6	20.4
1.5	33.1	9.6	4.7	9.2
2	26.8	9.1	3.9	9.2
2.5	23.5	9.6	4.7	9.2
3	20.9	8.6	3.7	8.6
3.5	19.4	7.9	3.2	8.2
4	18.7	7.0	3.0	8.6
4.5	17.4	6.9	2.9	7.6
5	17.7	5.7	1.9	10.2
5.5	16.0	5.7	2.1	8.2
6	14.6	5.4	2.4	6.7

**The conditions are same as Table A1*

Table A3 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at contact time of 500 g.h.mol^{-1}

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	52.5	13.8	1.6	37.1
1	35.1	19.8	2.4	12.9
1.5	33.6	19.7	2.9	10.9
2	31.1	17.2	1.4	12.5
2.5	27.3	15.4	1.0	10.8
3	28.8	19.9	2.0	6.9
3.5	25.8	18.8	1.9	5.1

4	25.7	19.2	1.8	4.7
4.5	25.2	17.9	1.5	5.9
5	24.1	15.8	1.2	7.1
5.5	20.2	14.7	1.2	4.3
6	17.8	13.3	2.1	2.5

**The conditions are same as Table A1*

A2: Effect of reaction temperature

Table A4 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at temperature of 165°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	2.87	2.00	0.32	0.55
1	2.72	1.92	0.30	0.50
1.5	2.12	1.47	0.26	0.39
2	1.98	1.40	0.27	0.31
2.5	1.92	1.43	0.23	0.26
3	1.71	1.24	0.19	0.28
3.5	1.69	1.22	0.27	0.20
4	1.62	1.20	0.20	0.22
4.5	1.59	1.18	0.17	0.23
5	1.41	0.94	0.15	0.32
5.5	1.36	0.98	0.16	0.22
6	1.16	0.84	0.14	0.17

Reaction condition; contact time: 360 g.h/mol, feed: 0.795 g/h of 5% wt. propionaldehyde, catalyst: 20% wt. Ni/SiO_2, ambient pressure, 60 mL/min of Nitrogen

Table A5 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at temperature of 180°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	7.08	4.87	0.75	1.47
1	7.04	4.66	0.56	1.82
1.5	6.94	5.01	0.53	1.40
2	6.93	4.07	0.46	2.41
2.5	6.83	5.08	0.62	1.13
3	6.77	4.29	0.51	1.96
3.5	6.65	3.02	0.71	2.92
4	6.51	3.73	0.51	2.27
4.5	6.34	4.06	0.58	1.70
5	6.31	3.17	0.47	2.67
5.5	6.27	4.44	0.60	1.23
6	6.13	4.21	0.51	1.41

**The conditions are same as Table A4*

Table A6 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at temperature of 195°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	40.53	22.58	2.02	15.93
1	23.42	14.12	1.59	7.71
1.5	22.64	13.11	1.50	8.03
2	20.79	11.45	1.39	7.95
2.5	18.62	10.26	1.24	7.12
3	17.57	11.35	1.17	5.05

3.5	17.90	12.20	1.12	4.59
4	15.59	10.68	1.09	3.82
4.5	14.82	10.26	0.97	3.59
5	12.89	9.16	0.83	2.89
5.5	12.88	9.68	0.78	2.43
6	11.01	7.16	0.66	3.19

**The conditions are same as Table A4*

Table A7 Conversion and yield obtained from water reduction of propionaldehyde over 20% wt. Ni/SiO_2 at temperature of 220°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	76.60	74.31	1.36	0.93
1	65.32	62.70	1.62	1.00
1.5	58.68	53.20	2.75	2.73
2	54.37	47.40	1.52	5.44
2.5	29.32	26.42	1.19	1.70
3	27.40	24.57	1.30	1.53
3.5	27.34	25.33	0.85	1.16
4	24.14	21.83	1.02	1.30
4.5	22.65	20.76	0.86	1.03
5	18.61	17.13	0.78	0.70
5.5	16.40	15.02	0.65	0.73
6	11.59	10.45	0.58	0.56

**The conditions are same as Table A4*

A3: Effect of Ni loadings

Table A8 Conversion and yield obtained from water reduction of propionaldehyde at temperature of 195°C and contact time 500 g.h.mol^{-1} over 5% wt. Ni/SiO_2

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	16.84	0.00	0.00	16.84
1	13.14	0.00	0.00	13.14
1.5	6.37	0.00	0.00	6.37
2	4.05	0.00	0.00	4.05
2.5	3.20	0.00	0.00	3.20
3	3.02	0.00	0.00	3.02
3.5	2.91	0.00	0.00	2.91
4	2.53	0.00	0.00	2.53
4.5	2.48	0.00	0.00	2.48
5	2.41	0.00	0.00	2.41
5.5	1.91	0.00	0.00	1.91
6	1.88	0.00	0.00	1.88

Reaction condition; temperature: 195°C, contact time: 500 g.h/mol, ambient pressure, feed: 0.795 g/h Propionaldehyde of 5% wt., 60 mL/min nitrogen

Table A9 Conversion and yield obtained from water reduction of propionaldehyde at temperature of 195°C and contact time 500 g.h.mol^{-1} over 10% wt. Ni/SiO_2

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	28.53	5.76	0.59	22.18
1	15.13	5.93	0.34	8.86
1.5	9.78	4.40	0.23	5.16
2	9.19	4.29	0.20	4.70

2.5	9.17	3.05	0.15	5.97
3	9.42	2.79	0.13	6.50
3.5	8.35	2.74	0.12	5.49
4	8.12	2.54	0.11	5.48
4.5	6.63	2.43	0.11	4.10
5	6.11	2.07	0.09	3.96
5.5	5.30	1.92	0.08	3.30
6	4.64	1.91	0.08	2.65

**The conditions are same as Table A8*

Table A10 Conversion and yield obtained from water reduction of propionaldehyde at temperature of 195°C and contact time 500 g.h.mol^{-1} over 15% wt. Ni/SiO_2

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	40.96	8.48	1.87	30.61
1	29.86	14.21	1.58	14.07
1.5	27.05	13.88	1.65	11.51
2	26.50	12.28	1.29	12.93
2.5	21.87	12.99	1.35	7.53
3	18.65	10.57	1.12	6.96
3.5	17.51	11.41	1.26	4.83
4	17.08	10.00	1.21	5.86
4.5	15.77	9.61	1.12	5.04
5	15.31	9.49	1.04	4.78
5.5	14.10	9.00	0.97	4.12
6	13.39	8.53	0.93	3.93

**The conditions are same as Table A8*

Table A11 Conversion and yield obtained from water reduction of propionaldehyde at temperature of 195°C and contact time 500 g.h.mol^{-1} over 20% wt. Ni/SiO_2

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	52.50	13.81	1.55	37.14
1	35.11	19.84	2.36	12.91
1.5	33.55	19.73	2.87	10.95
2	31.07	17.19	1.41	12.47
2.5	27.28	15.45	1.02	10.81
3	28.83	19.88	2.01	6.95
3.5	25.78	18.80	1.87	5.10
4	25.67	19.17	1.78	4.72
4.5	25.24	17.91	1.47	5.87
5	24.13	15.80	1.19	7.15
5.5	20.22	14.69	1.24	4.29
6	17.84	13.27	2.12	2.46

**The conditions are same as Table A8*

A4: Effect of reduction temperature

Table A12 Conversion and yield obtained from water reduction of propionaldehyde over 10% wt. Ni/SiO_2 at the reduction temperature of 360°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	26.62	6.63	0.63	19.35
1	14.56	4.58	0.34	9.64
1.5	12.64	3.30	0.19	9.15
2	11.50	3.97	0.24	7.29
2.5	10.92	3.90	0.26	6.76

3	10.58	3.59	0.20	6.79
3.5	9.01	3.15	0.17	5.69
4	8.36	2.78	0.14	5.44
4.5	7.54	3.03	0.15	4.37
5	7.21	2.16	0.12	4.96
5.5	7.23	2.04	0.11	5.07
6	7.22	3.15	0.15	3.93

Reaction condition; temperature: 195°C, contact time: 500 g.h/mol, ambient pressure, feed: 0.795 g/h Propionaldehyde of 5% wt., 60 mL/min nitrogen

Table A13 Conversion and yield obtained from water reduction of propionaldehyde over 10% wt. Ni/SiO_2 at the reduction temperature of 450°C

Time on steam (h)	Conversion (%)	Yield (%)		
		Ethylene	1-Propanol	Propionic acid
0.5	28.53	5.76	0.59	22.18
1	15.13	5.93	0.34	8.86
1.5	9.78	4.40	0.23	5.16
2	9.19	4.29	0.20	4.70
2.5	9.17	3.05	0.15	5.97
3	9.42	2.79	0.13	6.50
3.5	8.35	2.74	0.12	5.49
4	8.12	2.54	0.11	5.48
4.5	6.63	2.43	0.11	4.10
5	6.11	2.07	0.09	3.96
5.5	5.30	1.92	0.08	3.30
6	4.64	1.91	0.08	2.65

**The conditions are same as Table A12*